Electronic Supplementary Information (ESI)

Hydrophilicity and Oxophilicity of Isolated $CaMn_4O_5$ Cationic Cluster Modeling Inorganic Core of Oxygen-Evolving Complex

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Experimental Method

The stability and reactivity of calcium manganese oxide cluster ions, $Ca_mMn_nO_k^+$, were investigated using a reflectron-equipped time-of-flight mass spectrometer. Details of the experimental setup are shown in Figure S5. The $Ca_mMn_nO_k^+$ were generated using pulsed laser ablation inside a cluster source: A calcium metal rod and a manganese metal rod (Nilaco Co., Ltd., 99.99%) were vaporized using the focused second harmonic of Nd:YAG laser in the presence of oxygen diluted in helium at a stagnation pressure of 0.8 MPa. The formed $Ca_mMn_nO_k^+$ were passed through a reaction tube (4 mm diameter, 120 mm long), where they were heated. The temperature of the reaction tube was controlled from 300 to 1000 K by a resistive heater. The residence time of the cluster ions and the number density of the He gas in the extension tube were estimated to be longer than 100 s and 10^{18} cm^{-3}, respectively. The cluster ions were considered to achieve thermal equilibrium by collisions with the He carrier gas before expansion into the vacuum. When observing the reaction of the cluster ions with water, the He-diluted water vapor was introduced through a gas valve before expansion into the reaction tube for heating. (See Figure S5)

For the mass analysis, the $Ca_mMn_nO_k^+$ clusters were expanded into vacuum at the end of the extension tube and gained a kinetic energy of 3.5 keV in the acceleration region. After drifting in a 1 m field-free region, the cluster ions were reversed by a dual-stage reflectron, and were detected with a Hamamatsu double-microchannel plate detector. Signals from the detector were amplified with a 350 MHz preamplifier (Stanford SR445A) and digitized using an oscilloscope (LeCroy LT374). The mass resolution $m/\Delta m$ was ~1000, which was sufficient for estimating the ion intensity of each cluster.

Computational Method

The stable geometries and electronic structures of $CaMn_4O_k^+$, $Mn_4O_k^+$ and water complexes of them were obtained by quantum chemical calculations using Gaussian 09. Based on the results obtained by John P. Perdew et al. on the calculations of 3d transition metal[1] and the results of Dimitrios A. Pantazis et al. on the modeling tetranuclear manganese clusters of PSII,[2] we applied the hybrid functional using the exchange functional of Tao, Perdew, Staroverov, and Scuseria (TPSSh). The Pople-style orbital basis set 6-311+G(d) was used for all atoms.[3][4] The smaller basis set 6-31G was initially applied for obtaining low-energy geometries of the calcium manganese oxide clusters from the randomly and manually set initial geometries for reducing computational costs.[5] Then the low-energy geometries of the clusters with water were obtained by attaching a water molecule or a hydrogen atom and a hydroxide group randomly on the low-energy geometries of the calcium manganese oxide clusters. The geometries with energies up to +0.4 eV compared with the most stable geometry were also reoptimized with larger basis set as a comparison. The first, second and third lowest spin multiplicities were investigated during the calculations and some spin isomers with the similar geometries were obtained during the calculation, and here the most stable isomer was adopted.

[1] F. Furche, J. P. Perdew, *J. Chem. Phys.* **2006**, *124*, DOI 10.1063/1.2162161.
[2] D. A. Pantazis, M. Orio, T. Petrenko, S. Zein, E. Bill, W. Lubitz, J. Messinger, F. Neese, *Chem. - A Eur. J.* **2009**, *15*, 5108–5123.
[3] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650–654.
[4] D. Faron, P. Skurski, I. Anusiewicz, *J. Mol. Model.* **2019**, *25*, DOI 10.1007/s00894-018-3901-7.
[5] K. Yamamoto, K. Takatsuka, *Phys. Chem. Chem. Phys.* **2018**, *20*, 6708–6725.

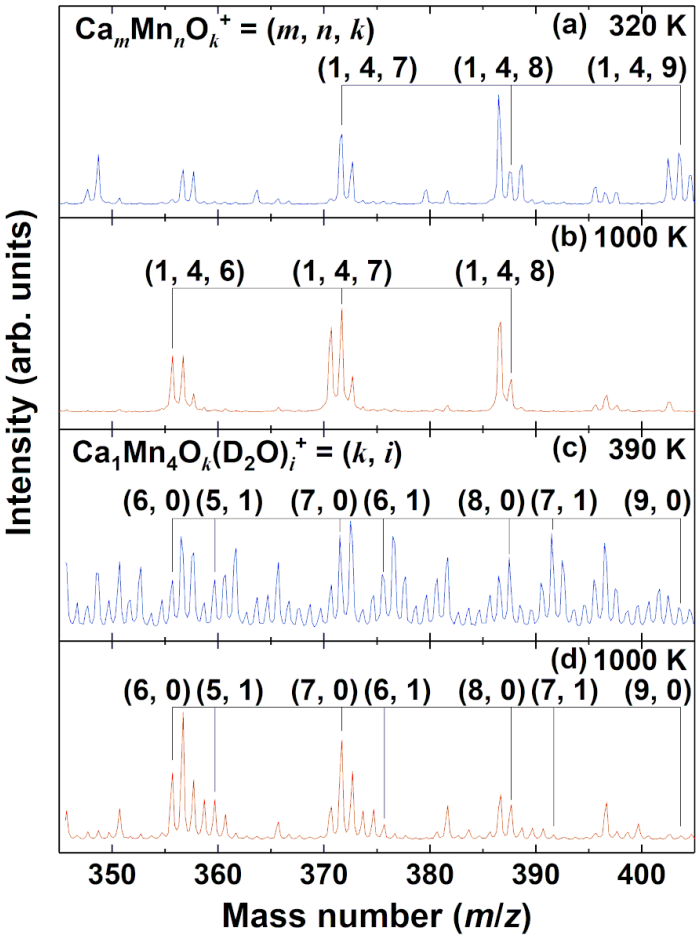


Figure S1. Mass spectra of $Ca_mMn_nO_k^+$ and water attached clusters at different temperatures.

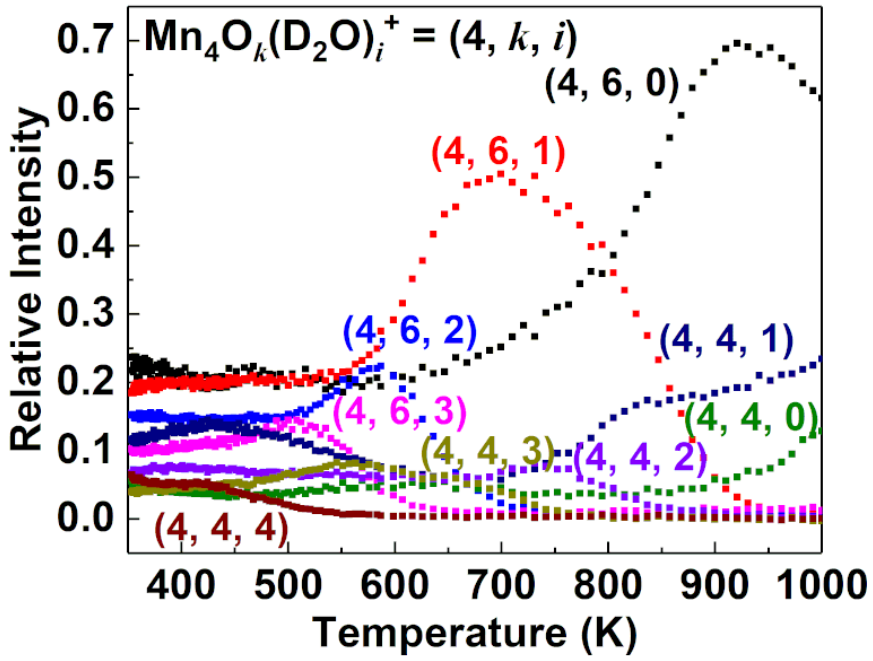


Figure S2. TDS plot of $Mn_4O_k^+$ clusters with water in the temperature range of 350–1000 K.

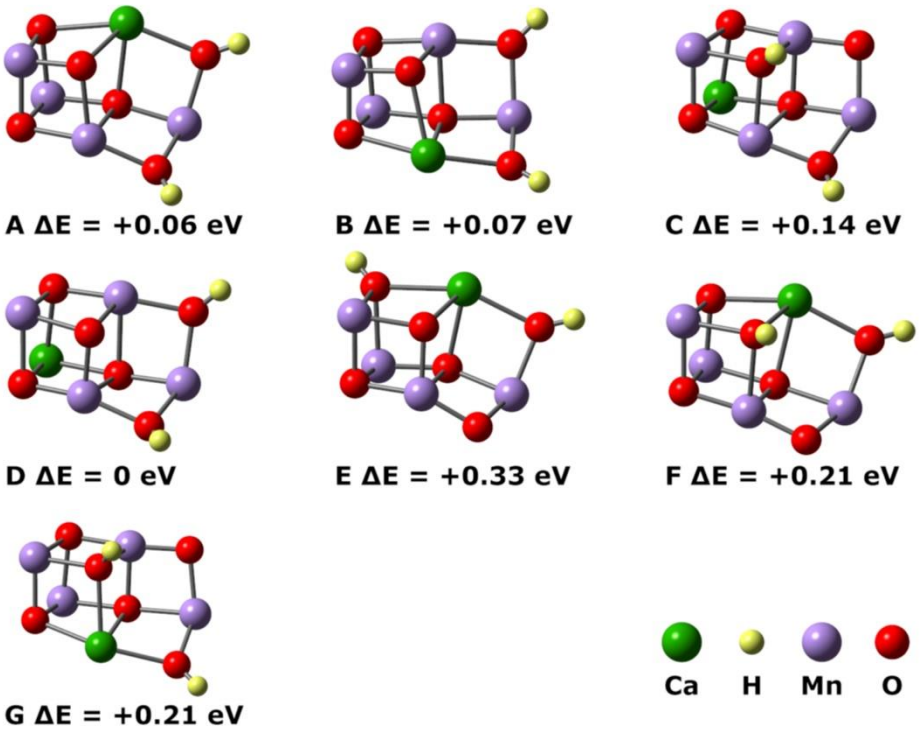


Figure S3. Several stable geometries of $CaMn_4O_4(OH)_2^+$. The geometries with the spin state of 20 are most stable in the spin isomers.

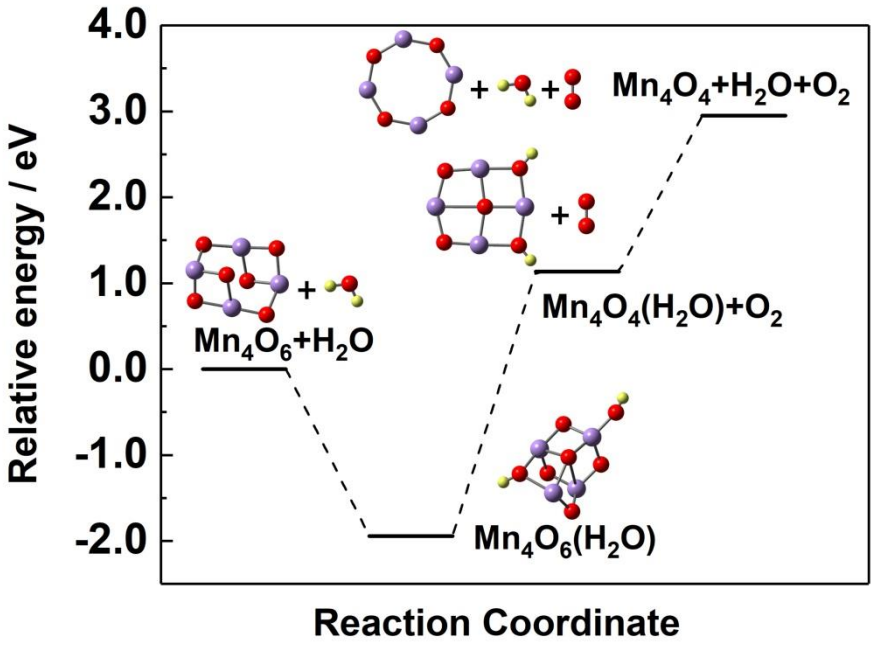


Figure S4. Energy diagram for forming $Mn_4O_4^+$ from $Mn_4O_6^+$ in the reaction with water.

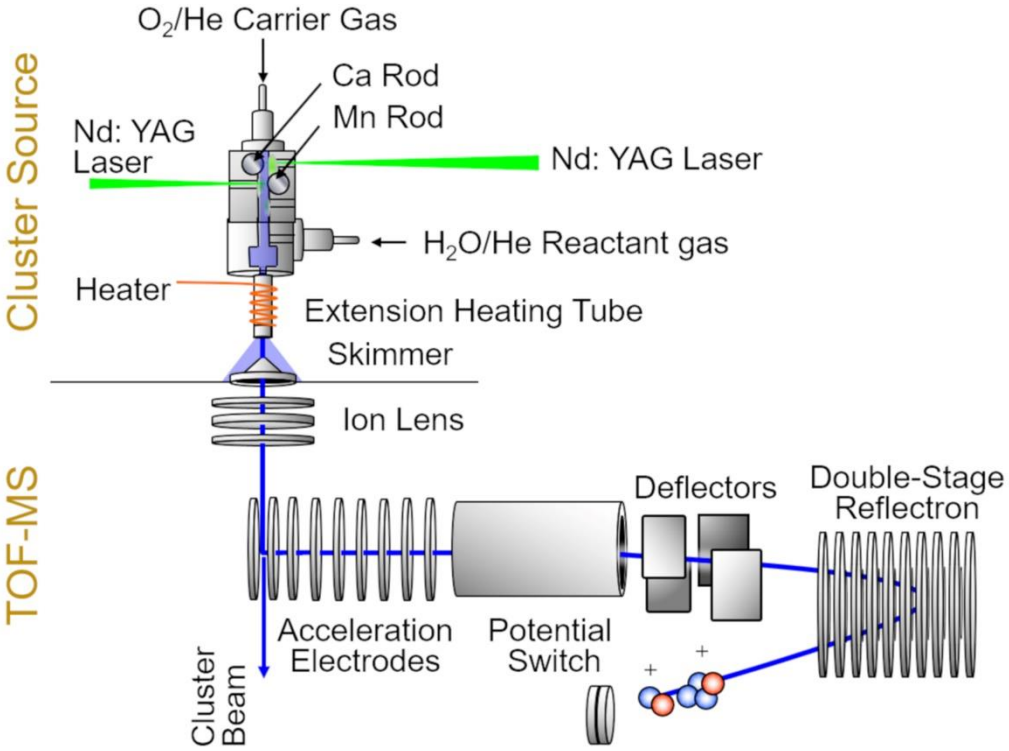


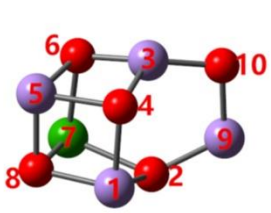
Figure S5. Schematic figure of experimental setup.

Table S1. Natural charges of atoms in $CaMn_4O_{5,7}^+$ and $CaMn_4O_4(OH)_2^+$ clusters. Following figure shows numbers labelled on atoms.

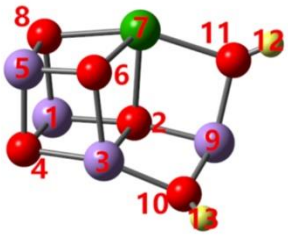
Number	$CaMn_4O_5^+$	Charge	$CaMn_4O_4(OH)_2^+$	Charge	$CaMn_4O_7^+$	Charge
1	Mn	1.31	Mn	1.34	Mn	1.41
2	O	-1.40	O	-1.37	O	-1.10
3	Mn	1.25	Mn	1.25	Mn	1.39
4	O	-1.06	O	-1.15	O	-0.92
5	Mn	1.30	Mn	1.26	Mn	0.83
6	O	-1.18	O	-1.05	O	-0.94
7	Ca	1.83	Ca	1.84	Ca	1.86
8	O	-1.33	O	-1.11	O	-0.92
9	Mn	1.33	Mn	1.38	Mn	1.21
10	O	-1.03	O	-1.13	O	-0.82
11			O	-1.24	O	-0.79
12			H	0.49	O	-0.22
13			H	0.50		

Local spin magnetic moments of Mn and O atoms. in $CaMn_4O_{5,7}^+$ and $CaMn_4O_4(OH)_2^+$ clusters. Following figure shows numbers labelled on atoms.

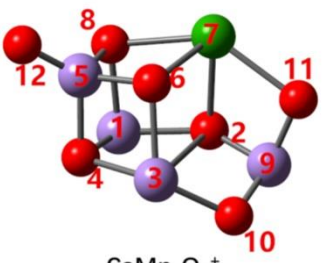
Number	$CaMn_4O_5^+$	Moment	$CaMn_4O_4(OH)_2^+$	Moment	$CaMn_4O_7^+$	Moment
1	Mn	4.66	Mn	4.68	Mn	4.68
2	O	0.24	O	0.29	O	0.19
3	Mn	3.76	Mn	4.68	Mn	4.71
4	O	0.21	O	0.38	O	0.21
5	Mn	4.71	Mn	3.76	Mn	1.86
6	O	0.17	O	0.11	O	0.16
7	Ca	0.01	Ca	0.01	Ca	0.01
8	O	0.27	O	0.15	O	0.17
9	Mn	4.71	Mn	4.73	Mn	2.85
10	O	0.25	O	0.12	O	0.10
11			O	0.75	O	0.12
12			H	0.01	O	-0.05
13			H	0.01		



$CaMn_4O_5^+$



$CaMn_4O_4(OH)_2^+$



$CaMn_4O_7^+$